

# Theoretical Studies of Possible Synthetic Routes for the High Energy Density Material $T_d N_4$ : Excited Electronic States

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## Abstract

Vertical electronic excitation energies for singlet states have been computed for the high energy density material (HEDM)  $T_d N_4$  in order to assess possible synthetic routes that originate from excited electronic states of  $N_2$  molecules. Several *ab initio* theoretical approaches have been used, including complete active space self-consistent field (CASSCF), state averaged CASSCF (SA-CASSCF), singles configuration interaction (CIS), CIS with second-order and third-order correlation corrections [CIS(D) and CIS(3)], and linear response singles and doubles coupled-cluster (LRCCSD), which is the highest level of theory employed. Standard double zeta polarized (DZP) and triple zeta double polarized (TZ2P) one-particle basis sets were used. The CASSCF calculations are found to overestimate the excitation energies, while the SA-CASSCF approach rectifies this error to some extent, but not completely. The accuracy of the CIS calculations varied depending on the particular state, while the CIS(D), CIS(3), and LRCCSD results are in generally good agreement. Based on the LRCCSD calculations, the lowest six excited singlet states are 9.35(1  $^1T_1$ ), 10.01(1  $^1T_2$ ), 10.04(1  $^1A_2$ ), 10.07(1  $^1E$ ), 10.12(2  $^1T_1$ ), and 10.42(2  $^1T_2$ ) eV above the ground state, respectively. Comparison of these excited state energies with the energies of possible excited states of  $N_2+N_2$  fragments, leads us to propose that the most likely synthetic route for  $T_d N_4$  involving this mechanism arises from combination of two bound quintet states of  $N_2$ .

## Introduction

High energy density materials (HEDMs) as potential novel fuels are of significant interest to the propulsion community. In particular, NASA is interested in developing a stable fuel that would allow single stage to orbit, as this would significantly reduce the cost of attaining Earth orbit. Tetrahedral ( $T_d$ )  $N_4$ , or tetrazete, is one such molecule that has been identified through theoretical studies as a possible HEDM mono-propellant fuel (see Refs. [1-7], and references therein). Theoretical calculations [1-3] have predicted a large energy difference between the tetrahedral form of  $N_4$  and two  $N_2$  molecules (186 kcal/mol; 8.07 eV), indicating that  $T_d N_4$  would be a high energy density species. These high-level *ab initio* calculations [1,5] have also shown that the barrier to dissociation along the singlet potential energy surface is very high ( $\approx$  60 kcal/mol; 2.60 eV). In addition, the only other possible dissociation channel, through spin-orbit coupling to the lowest triplet

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electronic state, has been shown [1,4] to require at least 13 kcal/mol (0.56 eV) activation energy, suggesting that  $T_d N_4$  will be sufficiently stable provided that it can be made. Having demonstrated that  $T_d N_4$  is a promising HEDM candidate, all that remained was to find a plausible synthetic route and then to provide a means of identifying it once made. The latter problem was in fact addressed in our earlier study [1] of  $T_d N_4$  where the harmonic vibrational spectrum was predicted using theoretical methods that have been shown [8] to yield very accurate transition frequencies. Unfortunately, the high-level calculations also showed that the one infrared (IR) active mode (a triply degenerate vibration) has a relatively small IR intensity, being only 12 km/mol (for comparison, the IR intensities of the O-H stretches in  $H_2O$  are between 50-70 km/mol). Perera and Bartlett [7], who also found a small IR intensity for the  $t_2$  vibrational mode, have recently computed the Raman intensities of  $T_d N_4$  and found these to be within a factor of three or four of the most intense  $H_2O$  mode for the  $a_1$  and  $t_2$  modes of  $T_d N_4$ .

Finding a plausible synthetic route, however, has proved difficult, which is not surprising since  $T_d N_4$  is a metastable compound. A brute force approach is simply to create a high-energy plasma of  $N_2$  molecules and then try to quench any  $T_d N_4$  that may have formed. Zheng *et al.* have recently [9] reported such a study and they have observed IR spectra consistent with  $T_d N_4$  formation. However, upon complete  $^{15}N$  isotopic substitution, they observed a shift that is somewhat inconsistent with theory,  $36.7\text{ cm}^{-1}$  from experiment vs.  $31.6\text{ cm}^{-1}$  from theory. Additionally, they were unable to observe bands attributable to  $T_d N_4$  in Raman spectra and mixed  $^{14}N$  and  $^{15}N$  isotopomers were not observed in the IR spectra. Since observation of the pure isotopomers was already near the instrument limitations, this latter problem could be due to the sharing of the IR intensity among multiple bands that occurs when the symmetry of the molecule is reduced from  $T_d$ . Depending on the particular mixed isotopomer, the symmetry will be either  $C_{3v}$  or  $C_{2v}$ . For example, using the CCSD(T)/[4s3p2d1f] data from Ref. [1], we find that for both  $C_{3v}$  isotopomers, the triply degenerate mode splits into doubly degenerate and nondegenerate modes with IR intensities that are approximately two thirds and one third, respectively, that of the parent isotopomer [10]. For the  $C_{2v}$  isotopomer, the situation is even worse since the triply degenerate mode splits into three nondegenerate vibrations all with approximately one third the original IR intensity. In the end, Zheng *et al.* concluded that further study was needed to confirm definitively that they had made  $T_d N_4$ .

The purpose of the present study is to investigate possible synthetic routes for  $T_d N_4$ , specifically those that arise from combining two  $N_2$  molecules in excited electronic states. We have started by examining vertical excitation energies (VEEs) for  $T_d N_4$  in order to see if any of these states correlate with and are lower in energy than appropriate combinations of two  $N_2$  molecules in excited electronic states. The theoretical methods used in this study are detailed in the next section, while the results are presented in the following section. Conclusions are given in the final section.

## Theoretical Approach

Three one-particle basis sets were used in these studies, the smallest of which is the standard Dunning-Huzinaga [11,12] double zeta plus polarization (DZP) basis set.

The polarization exponent for this basis is  $\alpha_d = 0.80$  and all six Cartesian components were included. The second basis set consist of the standard Dunning [13] (5s3p) triple zeta basis set augmented with two sets of polarization functions (TZ2P), and all six Cartesian components were again included. The orbital exponents for the latter polarization functions were taken from Ref. [14]. In order to test for Rydberg character, the TZ2P basis set was augmented with a set of diffuse *s* and *p* functions, with orbital exponents of 0.0674 and 0.0496, respectively, and will be designated TZ2P+. These orbital exponents were determined with the procedure outlined in Ref. [15].

Several theoretical approaches have been used for the determination of VEEs. Configuration interaction including only single excitations (CIS), also known as the Tamm-Dancoff approximation, represents the lowest level of theory and can be thought of as roughly equivalent to Hartree-Fock theory for excited electronic states. The CIS(D) approach [16] includes a correlation correction via second-order perturbation theory, and represents perhaps the simplest excited state method that includes the effects of dynamic electron correlation. The CIS(3) method [17] incorporates a third-order perturbation theory correction. The highest level of theory employed here is the linear-response singles and doubles coupled-cluster method (LRCCSD), which is equivalent to equations of motion CCSD (EOM-CCSD). Several studies using LRCCSD indicate that LRCCSD VEEs are accurate to about  $\pm 0.1$  eV provided the excited state is dominated by single excitations away from the reference state, or in other words that the summed weight of the single excitations is around 0.70 or higher (see Ref. [17] for a more detailed discussion).

For comparison purposes, the complete active space self-consistent field (CASSCF) approach has also been used. In these calculations, a 12 in 12 CASSCF was used, which includes the nitrogen 12 valence *p* electrons and *p*-like molecular orbitals in the active space. For the DZP basis set, the state averaged CASSCF (SA-CASSCF) procedure included the lowest sixteen roots (which, accounting for degeneracies, includes the lowest seven electronic states) with equal weights, whereas for the TZ2P basis set, only the lowest ten roots (five electronic states) were included.

All calculations have been performed at the CCSD(T)/ANO[432] optimized geometry from [1] and the nitrogen 1s-like core molecular orbitals have been held doubly occupied. The CASSCF and SA-CASSCF calculations were performed with the MOLPRO program package [18], while all of the other calculations have been performed with a modified [17] version of the TITAN [19] coupled-cluster programs.

## Results and Discussion

### A. Vertical Excitation Energies

The CASSCF and SA-CASSCF vertical excitation energies are reported in Table 1. The differences between results obtained with the DZP and TZ2P basis sets are relatively small, but unfortunately, the differences between the CASSCF and SA-CASSCF VEEs are much more significant and indicate that the lack of dynamic electron correlation is problematic. The order of the excited states does not change between these two approaches, and indeed, as will be evident from later results, the order of the states is consistent with that found at the LRCCSD level of theory. The CASSCF and SA-

CASSCF VEEs are reliable enough to indicate that the lowest excited singlet electronic state of  $T_d N_4$  is quite high in energy, occurring at 9.96 eV at the SA-CASSCF/TZ2P level of theory.

Table 2 contains the VEE values obtained with the CIS, CIS(D), CIS(3), and LRCCSD methods using the TZ2P basis set, while Table 3 contains VEEs determined with the TZ2P+ basis set. Comparison of the results in Tables 2 and 3 indicates that only the 5th and 6th excited states,  $2^1T_1$  and  $2^1T_2$ , exhibit a small degree of Rydberg character. We are thus confident that the TZ2P+ basis set has sufficient diffuse character to describe the excited electronic states under investigation.

Since comparison of the methods used in Tables 2 and 3 is similar for both the TZ2P and TZ2P+ basis sets, we discuss here only those results in Table 3, but we note that the results in Table 2 are important in order to establish the degree of Rydberg character. Not surprisingly, the CIS approach performs poorly for computation of VEEs, and in fact it obtains several states out of order in comparison to the LRCCSD VEEs. The CIS(D) VEEs are a marked improvement over the CIS values, although there are two states that are still in the wrong order (according to the LRCCSD results), albeit the two sets of states involved are very close in energy, having separations of only 0.03 eV and 0.05 eV at the LRCCSD level of theory. In comparison to LRCCSD, the CIS(D) VEEs are generally within about 0.15 eV except for the  $1^1T_1$  state for which the difference is 0.31 eV. Unfortunately, this difference is not systematic as the CIS(D) values are both higher and lower than the LRCCSD quantities, depending on the particular state.

The CIS(3) level of theory again is an improvement over the CIS(D) level, with the CIS(3) result being closer, compared to CIS(D), to the LRCCSD value for every state included in this study except for the  $2^1T_1$  state. Even for this state, however, the difference between CIS(3) and LRCCSD is only 0.05 eV. The CIS(3) VEE is within 0.07 eV of the LRCCSD value for every state except for the  $1^1T_1$  state, for which the difference is 0.16 eV. There are still two states out of order at the CIS(3) level of theory, however, this is at least in part due to the fact that there are four states within a 0.11 eV range. The excellent agreement between CIS(D), CIS(3), and LRCCSD indicates that all of these states are well described using single-reference based excited electronic state approaches, while the lack of agreement between the SA-CASSCF and LRCCSD VEEs shows the importance of including the effects of dynamic electron correlation. The large weight of the singles amplitudes in the LRCCSD procedure (see Tables 2 and 3) substantiates the conclusion that single-reference based approaches should perform well for these specific electronic states.

Our best results in Table 3 show that the lowest excited singlet electronic state of  $T_d N_4$  lies 9.35 eV higher in energy, which is a significant energy gap. There is then a cluster of four excited electronic states between 10.01 eV and 10.12 eV, which makes this region of its electronic spectrum somewhat congested. The large energy gap between the ground and first excited singlet state indicates that  $T_d N_4$  will be stable with respect to photodissociation under normal circumstances, since radiation that high in energy is not common at the Earth's surface [20]. In addition, this large energy gap has implications for the synthesis of  $T_d N_4$ . That is, the formation of  $T_d N_4$  via combination of two  $N_2$  molecules in excited electronic states should be more easily accomplished since competition from excited electronic states of  $T_d N_4$  will be minimal. This aspect is

discussed further in the following section.

## B. Correlation with N<sub>2</sub> Excited States

Figure 1 shows an energy correlation diagram between the electronic states of  $T_d$  N<sub>4</sub> and that of combinations of two excited state N<sub>2</sub> molecules that are singlet coupled. All possible singlet coupled combinations have not been included. For example, we have limited this diagram to include only the lowest few excited states of a particular spin since radiative relaxation will otherwise be a major loss mechanism, and we have excluded all repulsive states as well. In addition, singlet coupled excited state combinations above 20 eV have not been included except for specific cases which will be discussed below. The choice of N<sub>2</sub> states to be included in Figure 1 was determined based on the extensive data in Ref. [21] and also based on an extensive set of new *ab initio* calculations that will be published in due course [22]. Appropriate symmetry labels for the  $C_{2v}$  point group are included so that asymptotes that connect are apparent. The  $C_{2v}$  labels were chosen since it is highly unlikely that the reaction path to  $T_d$  N<sub>4</sub> formation would have higher symmetry, and lower point group labels are easily identified from the  $C_{2v}$  labels. The  $C_{2v}$  symmetry labels were determined by direct product of the resolution of the two linear N<sub>2</sub> molecules into  $C_{2v}$  symmetry with the  $z$  axis becoming the  $x$  axis for one N<sub>2</sub> and  $y$  for the other, or vice versa. In some cases, either the  $^1B_1$  or  $^1B_2$  state will exist, depending on the choice of axes, but not both, while in others both states appear. The interested reader is referred to Ref. [23] for further details on resolving the symmetry labels.

Examination of Figure 1 shows that there are a number of combinations of two excited state N<sub>2</sub> molecules that are both higher in energy and correlate with  $T_d$  N<sub>4</sub>. However, this alone does not mean that such a combination of two excited state N<sub>2</sub> molecules will lead to formation of  $T_d$  N<sub>4</sub>, since many of the excited singlet and triplet states still possess a multiple N=N bond. Formation of  $T_d$  N<sub>4</sub> from N<sub>2</sub> molecules in these states would require significant internal rearrangement of the electronic structure since  $T_d$  N<sub>4</sub> contains six single bonds [1], but no multiple bonds. Therefore, from this simple argument, the most likely formation mechanism for  $T_d$  N<sub>4</sub> will arise from two N<sub>2</sub> molecules that possess N-N single bonds and where all of the other valence  $p$  electrons are unpaired and accessible for formation of additional N-N single bonds. In fact, all of the bound low lying singlet and triplet states of N<sub>2</sub> possess N=N multiple bonds, and higher lying singlet and triplet states are susceptible to radiative relaxation to these states. From this consideration then, it would seem that the most likely formation mechanism for  $T_d$  N<sub>4</sub> from two N<sub>2</sub> molecules in excited electronic states should arise from bound quintet states, which possess only single N-N bonds.

Figure 2, constructed from data from Ref. [22], displays two quintet states,  $A' ^5\Sigma_g^+$  and  $C'' ^5\Pi_u$ , along with those singlet and triplet states that possess equilibrium bond lengths consistent with an N-N single bond. Note that the equilibrium bond length for these states is in the range of 1.4 to 1.6 Å, which is significantly longer than ground state N<sub>2</sub>. While we have included singlet and triplet states in Figure 2 and their energy correlations in Figure 1, we emphasize that the quintet states should be longer lived and therefore are of more interest with regard to synthesis of  $T_d$  N<sub>4</sub>. The bound  $A' ^5\Sigma_g^+$  state is relatively long lived since radiative decay is a much slower process owing to the need to include spin-orbit coupling, while the  $C'' ^5\Pi_u \rightarrow A' ^5\Sigma_g^+$  transition makes up the well

known Herman infrared system (see Refs. [24-26] and references therein for further discussion on possible production schemes for the quintet states). One potential difficulty in the formation of  $T_d N_4$  from two quintet states, or indeed from any combination of two  $N_2$  molecules in an excited state depicted in Figure 2, is the significant amount of internal energy that will need to be dissipated. For example, the  $A'^5\Sigma_g^+ + A'^5\Sigma_g^+$ ,  $A'^5\Sigma_g^+ + C''^5\Pi_u$ , and  $C''^5\Pi_u + C''^5\Pi_u$  asymptotes are 11.47, 13.29, and 15.11 eV, respectively, above  $T_d N_4$  in energy. However, it may be possible for the two  $N_2$  molecules in quintet states to first form an excited state of  $T_d N_4$  and then radiatively relax to ground state  $T_d N_4$ . The energy correlation diagram in Figure 1 shows that in this case significantly less internal energy would then need to be dissipated through molecular collisions. The potential for this latter mechanism, that is formation of  $T_d N_4$  in an excited electronic state from association of two quintet state  $N_2$  molecules, requires further exploration of the  $T_d N_4$  excited state potential energy surfaces, and the results of these studies will be reported in due course.

## Conclusions

The excited electronic states of  $T_d N_4$  have been investigated using ab initio theoretical methods in order to explore possible synthetic routes that originate from the combination of two  $N_2$  molecules in excited electronic states. Vertical excitation energies for  $T_d N_4$  have been computed at several levels of theory and good agreement is found between the CIS(D), CIS(3), and LRCCSD approaches. Based on the fact that all of the excited state wave functions are dominated by a single excitation away from the reference function, we expect our best results to be accurate to within  $\pm 0.1$  eV. Our best results from the LRCCSD/TZ2P+ level of theory are: 9.35(1  $^1T_1$ ), 10.01(1  $^1T_2$ ), 10.04(1  $^1A_2$ ), 10.07(1  $^1E$ ), 10.12(2  $^1T_1$ ), and 10.42(2  $^1T_2$ ) eV.

Based on the electronic structure of  $T_d N_4$ , it is argued that the most likely mechanism for formation from two excited state  $N_2$  molecules will involve excited electronic states of  $N_2$  that possess N-N single bonds rather than N=N multiple bonds. It is argued further than singlet and triplet states of  $N_2$  that exhibit this characteristic are susceptible to radiative decay to lower-lying singlet and triplet states which possess N=N multiple bonds and that therefore the most likely mechanism of this type will involve bound quintet states of  $N_2$ . We have identified two such states and have shown, based on an energy correlation diagram including symmetry considerations, that the association of two quintet state  $N_2$  molecules could end up in either the ground state or an excited electronic state of  $T_d N_4$ . The dissipation of residual internal energy may be a problem, but this could potentially be significantly reduced if formation in an excited state of  $T_d N_4$  occurs followed by radiative relaxation to ground state  $T_d N_4$ . Further studies of the excited state potential energy surfaces are planned in order to explore this possibility.

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Table 1.  $T_d N_4$  Vertical Excitation Energies (eV).<sup>a</sup>

State	main excitation	CASSCF <sup>b</sup>		SA-CASSCF <sup>b</sup>	
		DZP	TZ2P	DZP	TZ2P
X <sup>1</sup> A <sub>1c</sub>		0.857 865 63	0.882 995 75	0.838 841 11	0.866 248 35
1 <sup>1</sup> T <sub>1</sub>	(e→t <sub>1</sub> )	11.06	11.18	10.00	9.96
1 <sup>1</sup> T <sub>2</sub>	(e→t <sub>1</sub> )	12.56	12.68	11.13	11.14
1 <sup>1</sup> A <sub>2</sub>	(t <sub>2</sub> →t <sub>1</sub> )	13.86	14.01	11.49	11.61
1 <sup>1</sup> E	(t <sub>2</sub> →t <sub>1</sub> )	14.25	14.40	11.87	12.00
2 <sup>1</sup> T <sub>1</sub>	(t <sub>2</sub> →t <sub>1</sub> )	14.29	14.42	12.02	
2 <sup>1</sup> T <sub>2</sub>	(e→t <sub>2</sub> )	14.68	14.80	13.31	

<sup>a</sup> Using the CCSD(T)/ANO[432] ground state geometry given in Ref. [1].

<sup>b</sup> See text for description of the CASSCF active spaces used.

<sup>c</sup> Ground state energies are given as  $-(217+E)$  Hartree.



Table 2.  $T_d$  N<sub>4</sub> Vertical Excitation Energies (eV).<sup>a</sup>

State	main	CIS	CIS(D)	CIS(3)	LRCCSD	
	excitation				Energy	wgt. <sup>b</sup>
1 <sup>1</sup> T <sub>1</sub>	(e→t <sub>1</sub> )	9.06	9.67	9.51	9.36	0.833
1 <sup>1</sup> T <sub>2</sub>	(e→t <sub>1</sub> )	10.61	9.96	10.04	10.03	0.790
1 <sup>1</sup> A <sub>2</sub>	(t <sub>2</sub> →t <sub>1</sub> )	11.23	9.88	10.12	10.05	0.767
1 <sup>1</sup> E	(t <sub>2</sub> →t <sub>1</sub> )	10.54	10.21	10.11	10.09	0.813
2 <sup>1</sup> T <sub>1</sub>	(t <sub>2</sub> →t <sub>1</sub> ) <sup>c</sup>	10.25	10.39	10.30	10.26	0.825
2 <sup>1</sup> T <sub>2</sub>	(e→t <sub>2</sub> )	11.49	10.74	10.83	10.66	0.812

<sup>a</sup> Using the CCSD(T)/ANO[432] ground state geometry from Ref. [1], and the TZ2P basis set.

<sup>b</sup> Norm of singles amplitudes.

<sup>c</sup> Main excitation for the CIS state is (e→t<sub>2</sub>), though there is a considerable contribution from (t<sub>2</sub>→t<sub>1</sub>).

Table 3.  $T_d N_4$  Vertical Excitation Energies (eV).<sup>a</sup>

State	main excitation	CIS	CIS(D)	CIS(3)	LRCCSD	
					Energy	wgt. <sup>b</sup>
1 <sup>1</sup> T <sub>1</sub>	(e→t <sub>1</sub> )	9.05	9.66	9.51	9.35	0.836
1 <sup>1</sup> T <sub>2</sub>	(e→t <sub>1</sub> )	10.52	9.97	10.02	10.01	0.799
1 <sup>1</sup> A <sub>2</sub>	(t <sub>2</sub> →t <sub>1</sub> )	11.21	9.87	10.11	10.04	0.770
1 <sup>1</sup> E	(t <sub>2</sub> →t <sub>1</sub> )	10.52	10.19	10.09	10.07	0.817
2 <sup>1</sup> T <sub>1</sub>	(t <sub>2</sub> →t <sub>1</sub> )	10.10	10.13	10.07	10.12	0.858
2 <sup>1</sup> T <sub>2</sub>	(e→t <sub>2</sub> )	11.07	10.25	10.42	10.42	0.783

<sup>a</sup> Using the CCSD(T)/ANO[432] ground state geometry from Ref. [1], and the TZ2P+ basis set.

<sup>b</sup> Norm of singles amplitudes.

### Figure Captions

Figure 1. Energy correlation diagram between electronic states  $T_d N_4$  and combinations of two  $N_2$  molecules.

Figure 2. Potential curves for the ground electronic state of  $N_2$  and excited bound states that exhibit an equilibrium bond distance consistent with an N-N single bond.



